

The University of Chicago

THE PINACOL-PINACOLONE
MOLECULAR REARRANGEMENT:
THE REARRANGEMENT OF
PINACOL DIBROMIDE

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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FREDERICK H. ROBERTS

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The author wishes to express his gratitude to Professor Julius Stieglitz for his guidance during this investigation, and to thank Dr. R. W. Johnson and Dr. K. H. Adams for their helpful suggestions.

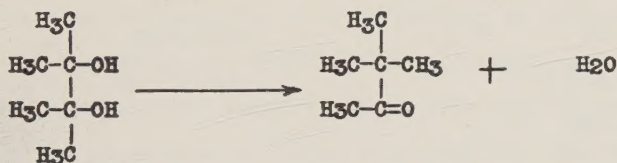


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I. INTRODUCTION

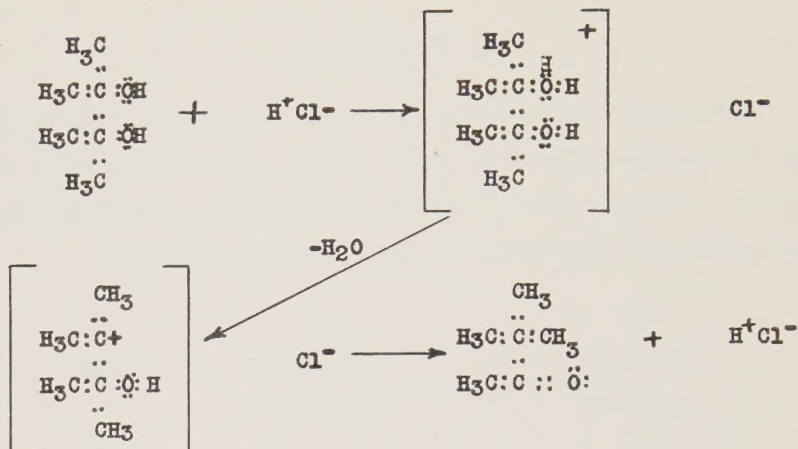
The pinacol-pinacolone molecular rearrangement which results in the formation of a ketone from a di-hydric tertiary alcohol is a case of intramolecular oxidation and reduction. The reaction may be represented by the following equation.



which indicates that the two adjacent carbinol carbon atoms in the molecule have been changed from their original state of partial oxidation. One atom appears completely reduced while the other is oxidized to the ketone stage. This state of partial oxidation constitutes a fault in the molecule¹ because it represents an unstable condition, Ostwald having pointed out many years ago that the intermediate oxides of an element (e.g. chloro-sulfur, phosphorus, etc.) tend to form, by intermolecular oxidation and reduction, the final products of reduction and of oxidation of the element in question. Acids are catalysts for the pinacol rearrangement shown above. It is believed that they cause the formation of an oxonium salt of pinacol, which is capable of losing a molecule of water, thus exposing an open

¹Theory of J. Stieglitz, reported in the Doctorate Dissertation of R. B. Cooper, The University of Chicago (1930); "Abstracts of Theses, The University of Chicago, Science Series" (1932) Vol. VIII, p. 77 (1929-30). Also see Doctorate Dissertations, The University of Chicago, of (a) G. W. Ayers (1931), K. H. Adams (1932).

positive position on one of the carbinol carbon atoms:



This free positive charge on the carbonium ion is considered capable of attracting a negative methyl group from the adjacent carbon atom. The hydrogen of the hydroxyl group then ionizes and the rearrangement is completed.

On the basis of this theory, it is evident that if there are no intervening conflicting reactions, any derivative of pinacol capable of giving the intermediate positive carbonium ion should undergo the pinacol-pinacolone rearrangement.

In support of this conclusion Adams¹ found that the amine, $(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{C}(\text{OH})(\text{CH}_3)_2$, corresponding to pinacol, forms ammonium salts which when heated undergo the pinacol type of rearrangement with loss of ammonia. In agreement with the greater stability of alkyl ammonium salts as compared with oxonium salts, these ammonium salts require higher temperatures to induce loss of the alkyl and bring about the opportunity for rearrangement than do the oxonium salts of the true pinacols. Brower² found that the

¹K. H. Adams, loc. cit.

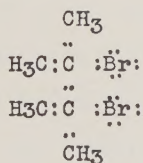
²Brower, Doctorate Dissertation, University of Chicago (1933).

similar anilide, $(\text{CH}_3)_2\text{C}(\text{NC}_6\text{H}_5)\text{C}(\text{OH})(\text{CH}_3)_2$, would rearrange under the conditions predicted.

Cooper, Adams, and Brower determined the velocity coefficients of the rearrangement with clarifying results.

Finally, Ayers¹, working with tetramethyl ethylene chlorohydrin, the bromohydrin, and the iodohydrin was successful in showing the increasing instability due to heat, and the tendency of the hydrins to rearrange in pinacol fashion as one goes from the chloro to the bromo and finally to the iodohydrin. The iodohydrin rearranges at room temperature to give pinacolone and the bromohydrin rearranges at lower temperatures than the chlorohydrin, in accordance with the theoretical forecast.

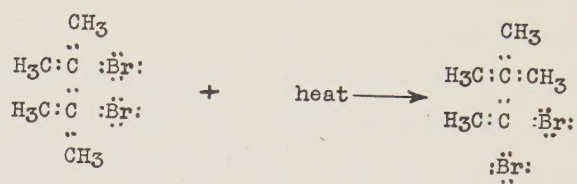
As a further test of this theory of the pinacol-pinacolone rearrangement the present investigation has been made under the direction of Professor Stieglitz on the possibilities of rearrangement of tetramethyl ethylene dibromide.



By selection of the dibromide the possible effect of the second hydroxyl group in pinacol and in the corresponding amines is eliminated.

With this work it was hoped to show that the symmetrical dibromo derivative of pinacol might rearrange upon being heated to give an unsymmetrical compound, pinacolone dibromide:

¹Ayers, loc. cit.



II. THEORIES OF PINACOL REARRANGEMENTS

Ever since the discovery of the pinacol rearrangement by Fittig¹ in 1859 many theories have been advanced to explain the change which takes place. These theories have been reviewed from the historical point of view very completely by Adams², Ayers³, and Brower.⁴ None of the older theories explains completely the process by which the postulated intermediates lose water and form the rearranging intermediate carbonium ion. In certain important instances there are partial similarities between older theories and the one under investigation.

The catalytic effect of acids upon this rearrangement has long been known and Stieglitz and Cooper⁵ measured the velocity coefficient of the rearrangement of pinacol itself under the influence of acids and have shown that the catalytic effect is directly proportional to the hydrogen ion concentration. This velocity varies with the nature of the catalyzing acid. The Stieglitz theory, which is presented below, takes into account this important fact of the activity induced by the hydrogen ion and gives a mechanism for the rearrangement.

¹Fittig, Ann. 110, 25 (1859); 114, 54 (1860).

²Adams, loc. cit.

³Ayers, loc. cit.

⁴Brower, loc. cit.

⁵Cooper, loc. cit.

The Stieglitz Theory

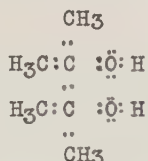
An electronic concept of the pinacol-pinacolone rearrangement follows directly from work on the electron theory of valence for the interpretation of the Beckmann and related rearrangements as well as intramolecular rearrangements in general.¹ Stieglitz² has found that the cause of the rearrangements of such compounds as triphenylmethyl halogen amines, hydroxylamine derivatives, hydrazides, azides and peroxides, is the presence of an unstable electronic condition around an atom in the molecule, which tends to go over to a more stable configuration. In every instance the tendency of the atom in question to absorb electrons from neighboring atoms in the original molecule is found to be satisfied in the reaction. It must be concluded that in all these cases the tendency mentioned and its satisfaction bring about the rearrangement. Thus with the halogen amine derivatives, it is the positive halogen atom with only six electrons in its valence shell, which is the unstable entity and it is its tendency to pick up two electrons, thereby completing its octet and forming stable negative halogen ion that brings about the rearrangement. These halogen amines, as well as the other substances mentioned above, present systems of atoms existing in intermediate states of oxidation, which, as Ostwald showed, are in an unstable condition. As a result of this instability of partially oxidized atoms the molecules often undergo intermolecular

¹The independent work of Stieglitz, J. Am. Chem. Soc., 36, 272 (1914) and L. W. Jones, Am. Chem. J., 50, 414 (1913) on the application of the electron theory of valence to molecular rearrangements was announced almost simultaneously.

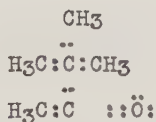
²Stieglitz, Proc. Nat. Acad. Sci., I, 205 (1915).

or intramolecular oxidation-reduction reactions by which the specific atom in question is oxidized (loses electrons) in some of the molecules of the compound and is reduced (gains electrons) in other molecules. Common instances of this principle are the changes of hypochlorites to chlorides and chlorates and sulfites to sulfides and sulfates.

If we examine the pinacol molecule we find it represents a case of instability since there are two adjacent tertiary carbinol carbon atoms in an intermediate stage of oxidation.



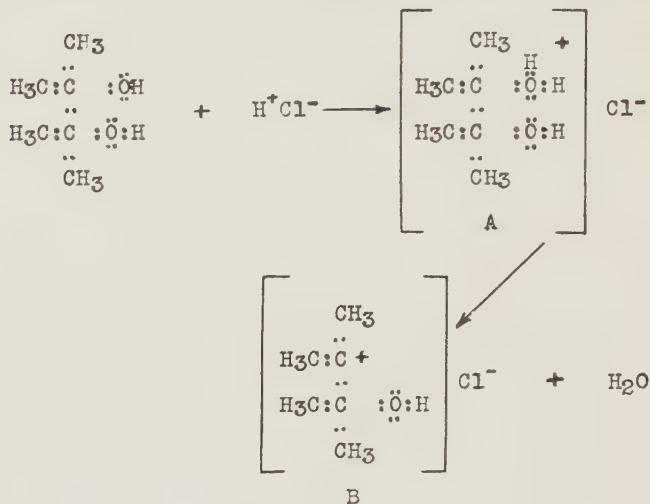
The electrons surrounding the carbinol carbon atoms are arranged :C : which is not as stable an arrangement as :C: , the completely reduced state, or as : C : , the completely oxidized state. In the product of the rearrangement, pinacolone,



one carbinol carbon atom has been fully reduced and its electron octet is complete, the other carbinol carbon atom has become as fully oxidized as is possible without losing electrons to some outside vigorous oxidizing agent. Thus it is evident that the pinacol-pinacolone rearrangement is a typical intra-molecular oxidation-reduction reaction.

If the Stieglitz theory of intramolecular oxidation-reduction contains an explanation of this rearrangement the reaction should take place in all cases in which the path is opened for

the free transference of electrons, or groups which are tightly bound to the electrons. The catalytic effect of acids upon the rearrangement of pinacol is primarily one of causing such an opening for the easy passage of electrons and the rearrangement is explained as follows: The primary function of acids is the formation of salts, hence with the weakly basic oxonium compound,



pinacol, an oxonium salt can be formed.¹ The cation of the oxonium compound, called A above, is capable of losing water and producing an intermediate compound, B, which is a carbonium ion, carrying a positive charge on what was a carbinol carbon atom. This entity possesses only momentary existence. Under ordinary conditions it would combine with the halogen ion forming the chlorohydrin, $(\text{CH}_3)_2\text{CClC}(\text{OH})(\text{CH}_3)_2$, in the same way as the oxonium salts of mono alcohols form alkyl halides. But in the present

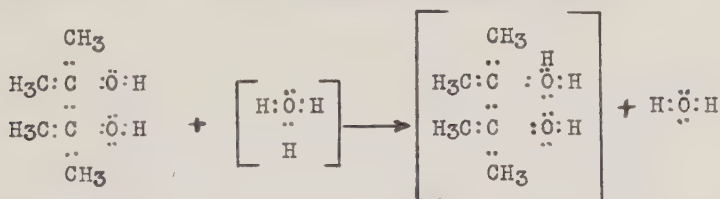
¹See Stieglitz theory of imido ester and ester catalysis by acids. Stieglitz, Am. Chem. J. 39, 29, 166 (1908). Stieglitz with Darby and McCracken, Am. Chem. J., 39, 402, 437 (1908).

instance the free positive charge on the carbon atom has an opportunity of attracting a negative methyl group from the neighboring carbinol carbon atom, which is much closer to it than is the chloride ion. After the migration of the $\text{H}_3\text{C:}$ group the hydrogen atom ionizes from the hydroxyl group and the rearrangement product is complete:



The oxonium salts of pinacol are not merely assumed intermediates, since pinacol hydrochloride has been isolated by Harries¹ and pinacol hydrobromide has been made in this laboratory by Ayers.² Pinacol is such a very weak base that the salts are very largely hydrolyzed in aqueous solution so the compound cannot be isolated from this medium. This idea is expressed by K. H. Adams,³

. . . . in a solution of pinacol in dilute acid there must be a distribution of the hydrogen ion of the acid between the molecules of water and of pinacol as demanded by the application of the law of chemical equilibrium to the case of the distribution of an acid between two weak bases.



The point of equilibrium is probably far toward the left, as the equation is written, due to the preponderance of water

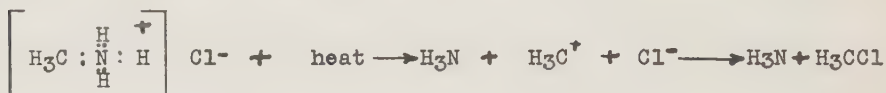
¹Harries, Ann., 383, 183 (1911).

²Ayers, loc. cit., pp. 38, 61.

³Adams, loc. cit., pp. 12-13.

molecules and possibly due to the greater stability of the hydronium ion as compared to the pinacol oxonium ion. Consequently, the concentration of the latter may be very small, but according to our theory it is this relatively small number of ions which constitutes the active mass in the rearrangement.

It was mentioned above that a consequence of this theory of the pinacol rearrangement is that any derivative of pinacol capable of producing the positive carbonium ion would be expected to give the pinacol rearrangement. Thus Adams¹ and Brower² have shown that the amines corresponding to pinacols form salts which when heated undergo the pinacol-pinacolone rearrangement. It is well known that when the hydrochloride of an alkyl amine such as methylamine, is heated ammonia is lost and methyl chloride is formed. Presumably the first action leads to the loss of ammonia and the formation of H_3C^+ which then combines with the chloride ion to form methyl chloride:



With higher, more complex, alkyl radicals, $\text{C}_n\text{H}_{2n-1}$ hydrogen ion is often lost and an olefine, C_nH_{2n} , formed before the carbonium ion can combine with the chloride ion. A perfect analogy is presented by the case of the carbonium ion of a pinacol in which a rearrangement (migration of a $\text{H}_3\text{C}:$ group) takes place before the carbonium ion can unite with the halogen ion.

In agreement with the known greater stability of alkyl ammonium salts as compared with alkyl oxonium salts, Adams and Brower found that the ammonium salts require higher temperatures

¹Adams, loc. cit.

²Brower, loc. cit.

to break off the alkyl groups and effect their rearrangement.

Acids are not always necessary for rearrangements of this type. Thus in the case of a halogen substituted pinacol, a halohydrin, $(\text{CH}_3)_2\text{C}(\text{Hal})\text{C}(\text{OH})(\text{CH}_3)_2$, heat is sufficient to activate the atoms and cause the halogen to leave the molecule with its full complement of electrons, a negative ion; this leads to the appearance of the open positive position on the tertiary carbon atom and rearrangement results. These halogen derivatives should rearrange more easily when heated than pinacol, since alkyl halides are far more active than alcohols in the carbon position. Thus Ayers¹ has found that pinacol iodohydrin rearranges at room temperature to give pinacolone.

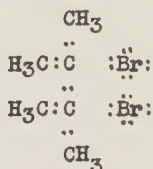
The present investigation of tetramethyl ethylene dibromide was undertaken to ascertain the action of heat and of silver oxide which, by producing the desired positive carbonium ion, might cause the rearrangement, in the absence of intervening destructive reactions.

¹Ayers, loc. cit.

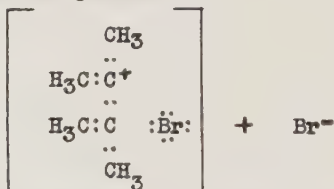
III. DISCUSSION OF THE RESULTS

Tetramethylethylene dibromide, $(\text{CH}_3)_2\text{CBrCBr}(\text{CH}_3)_2$, and its possible product of rearrangement, pinacolone dibromide, $(\text{CH}_3)_3\text{C-CBr}_2(\text{CH}_3)$, were each prepared by an improved method (See Experimental Part) and their chemical and physical properties were studied.

Pyrolysis of tetramethylethylene dibromide.- Tetramethylethylene dibromide fulfills the conditions stipulated by the Stieglitz theory for a compound which could display the pinacol-pinacolone type of rearrangement; that is, this compound is capable of giving a positive carbonium ion. By hydrolysis all of the bromine is converted into bromide ion and consequently each bromine atom has its full complement of eight electrons. The electronic structure of the dibromide is therefore



Heat might ionize it with the production of



provided other possible intervening reactions (such as the loss of hydrogen bromide to form olefines) did not interfere with the ob-

¹In bromomalonyl urea and certain other compounds we have relatively positive bromine atoms $:\ddot{\text{Br}}:$ attached to negative carbon.

jective aimed at.

The dibromide was selected in preference to the dichloride because the bromides are somewhat more reactive. At best, in view of an investigation by Meerwein,¹ it was expected that the amount of transformation would be very small. Meerwein reports that for several years he has tried to establish an isomeric equilibrium between pinacol dichloride and pinacolone dichloride,



but he was not successful in showing that a direct transformation of the one into the other exists. However, Meerwein does report that if the vapors of pinacolone dichloride are passed over barium chloride at 400°-450° a small amount, about 5 per cent, of 2,3,-dimethyl butadiene is formed which can only be explained through the assumption of a primary rearrangement of pinacolone dichloride into pinacol dichloride and of the latter into the butadiene.

It was thought that with the dibromide there would be a greater chance for activity since it is well known that in alkyl halides there is an increasing reactivity from the chlorine compounds to the iodine. Thus, the dibromide of pinacol should be less stable than the dichloride.

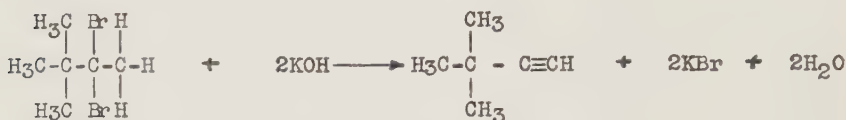
Efforts to effect a rearrangement of the symmetrical dibromide to the unsymmetrical and, thus to a pinacolone derivative, were carried out in anhydrous benzene and ether solutions at 150°-250°.

Detection of any rearrangement.- As both of the dibromo

¹Meerwein, Ann., 435, 191 (1923).

compounds are very volatile, identification by isolation of the rearrangement products was not attempted. Since the entire rearrangement mixture is present in a benzene solution hydrolysis of the respective dibromo compounds to pinacol and pinacolone by dilute aqueous sodium carbonate or sodium hydroxide solutions is very inefficient and in this case almost impossible because of the extreme insolubility of the compounds in water.

The unsymmetrical dibromide when treated with alcoholic potassium hydroxide in a bomb gives up two mols of hydrogen bromide and tertiary butyl acetylene is formed:¹



This acetylene is a stable compound and is not affected by alcoholic alkali when heated with it as high as 200°. It is capable of giving all the characteristic reactions of an acetylene and therefore may be detected either by its copper or silver salt precipitated from ammoniacal cuprous chloride or ammoniacal silver nitrate solution, respectively. The silver salt was used because it is less soluble than the copper acetylide. Trial runs with known samples of synthetic pinacolone dibromide were made and it was found possible to detect even extremely small amounts of the acetylene by means of its silver salt. This afforded a method of analyzing the contents of the bomb after pyrolysis of the symmetrical dibromide. If any of the unsymmetrical dibromo product is present due to rearrangement of pinacol dibromide it will be converted into the isobutyl acetylene by treatment of the entire mixture

¹Faworsky, *J. prakt. Chem.*, 37, 393 (1888); 88, 673 (1913).
 Couturier, *Ann. Chim. Phys.*, (6), 26, 450 (1892).
 Delacre, *Bull. Soc. Chim.* (Paris), (3), 35, 343 (1906).

with alcoholic potassium hydroxide.

When a benzene solution of pinacol dibromide was heated in bombs at 150°-250° and the contents of the bombs were then worked up as indicated with alcoholic potassium hydroxide, no evidence of the formation of tertiary butyl acetylene was found in any of the attempts. Consequently no rearrangement of pinacol dibromide to pinacolone dibromide or a derivative of it formed by the migration of a methyl group occurs. The pyrolysis of the pinacol dibromide evidently follows the same course as that of the dichloride, studied by Meerwein, which yielded 2,3 dimethyl butadiene. The contents of the bombs after they had been heated and then cooled, always gave off hydrogen bromide in quantity and yielded a substance which takes up bromine from a chloroform solution. The presence of lachrymatory products indicated also that compounds of the type $\text{BrCH}_2(\text{CH}_3)\text{CH}.\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$ are formed by absorption of some of the hydrogen bromide by butadiene derivatives. The desired dibromide $(\text{CH}_3)_3\text{C}-\text{CBr}_2(\text{CH}_3)$ is itself a powerful lachrymator but its absence has been shown by the failure to produce tertiary butyl acetylene. The pyrolysis of pinacol dibromide can follow these parallel reactions and evidently does so in preference to the rearrangement aimed at.

The rearrangement of pinacol dibromide by pyrolysis was also tried in an anhydrous ether solution saturated with hydrogen bromide which would tend to decrease its loss by the dibromide molecule. These bombs were heated to 150° but there was no evidence of rearrangement in any of the trials as judged by the tertiary butyl acetylene test of the products of pyrolysis.

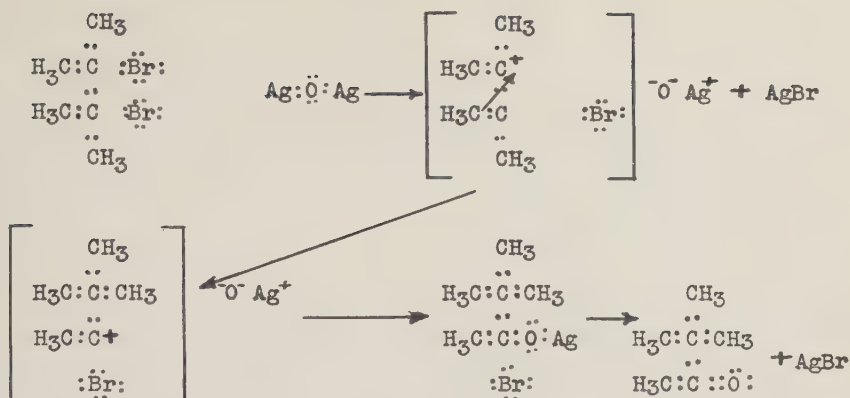
The results obtained show that there are very great differences in the mobility of the bromine atoms of the bromohydrine, $(\text{CH}_3)_2\text{C}(\text{OH})\text{CBr}(\text{CH}_3)_2$, and the dibromide, $(\text{CH}_3)_2\text{CBrCBrC}(\text{CH}_3)_2$, in spite of the similarity in their structures. The

presence of the hydroxyl group in the former naturally suggests that hydrogen bromide is first lost and that tetramethylethylene oxide is formed as a step in the rearrangement reaction. This has, however, been specifically proved not to be the case.¹ We would suggest that the greater mobility of the halogen in the bromohydrine may well be due to the action of the oxygen atom on the neighboring alkyl bromide group. Alkyl halides are dissociated by amines to form alkyl ammonium salts, and preceding the actual dissociation of the alkyl halide and recombination of its components with the amines there must be a strong loosening effect on the carbon-halogen bond, which is caused by the amines. Oxygen derivatives have a far weaker effect, but the tendency toward oxonium salt formation must exist and the oxygen of the hydroxyl group might thus contribute decisively to the ease with which the pinacol halohydrines lose their halogen atoms and undergo rearrangement as compared with our dibromide. In the pinacol dibromides there would be no such effect, the tendency to form bromonium² salts being extraordinarily slight.

Rearrangement of pinacol dibromide by silver oxide in anhydrous medium.- Pinacol dibromide was dissolved in dry ether and shaken with dry silver oxide at room temperature. This was done to cause one of the tertiary carbon atoms to lose two electrons and thus become relatively positive as indicated by the following outline:

¹K. H. Adams, loc. cit., pp. 3-6; G. W. Ayers, loc. cit., pp. 5-9.

²J. Stieglitz and E. E. Barnard, J. Am. Chem. Soc., 27, 1016 (1905).



With the formation of the positive carbonium 'A' there is an opportunity for migration of one of the methyl groups from the neighboring tertiary carbon atom, thus effecting the desired rearrangement.

Detection of rearrangement.- Silver oxide does cause a rearrangement of the molecule of pinacol dibromide. The pinacolone formed in the reaction can be detected by Nessler's reagent.¹ This conclusion may be confirmed by isolating the Nessler precipitate and recovering pinacolone from it by distillation with sulfuric acid. The distillate will give the semicarbazone derivative of pinacolone and it may be oxidized to trimethyl acetic acid for further identification.

There is another possible reaction between pinacol dibromide and silver oxide in which tetramethyl ethylene oxide is formed.



The presence of this oxide does not hinder the identification of

pinacolone by Nessler's reagent. Tetramethyl ethylene oxide reacts very slowly with water at room temperature to form the hydrate of pinacol.¹ Delacre has shown that this hydration is retarded in alkaline solution. Thus, in the presence of Nessler's solution, which is extremely alkaline, there is very little chance for pinacol formation. Any small amount of pinacol that may form does not change the amount of pinacolone in any way since Adams² has shown that rearrangement in alkali cannot be detected.

Quantitative estimation of pinacolone.- Because Nessler's reagent proved to be a very convenient means of detecting the presence of pinacolone under the conditions of these experiments, Cooper's³ method, with necessary modifications, was used for the quantitative determination of the ketone. This method is an empirical one and its usefulness depends upon a calibration curve made from the weights of Nessler's precipitate with known quantities of pinacolone since the weight of precipitate is not a straight line function of the amount of ketone present. The weights of the precipitates obtained are plotted against the concentrations of the respective solutions expressed in any convenient terms.

Because ether was used as a solvent for the pinacol dibromide in these determinations the concentrations of the standard pinacolone solutions were expressed as a weight composition. In this case weight per cent was used. This method was chosen because the ether could be handled and weighed in glass stoppered, Erlenmeyer flasks thus allowing a minimum of evaporation. When this calibration curve is obtained an analysis may be carried out

¹Delacre, Bull. Soc. Chim., (4), 3, 203 (1908); (4), 1, 586 (1907).

²Adams, loc. cit.

³Cooper, loc. cit.

on a pinacolone solution of unknown strength. The analysis must be carried with the observation of exactly the same conditions that prevailed when the calibration data were obtained. When the weight of Nessler's precipitate from a given solution is known the composition of the solution may be read from the calibration curve.

The state of subdivision of the silver oxide is an important factor in the extent of rearrangement. Since the reaction depends upon contact with the surface of the silver oxide the greater surface which it presents the further the action will proceed. Large particles become coated with silver bromide and become incapable of further reaction.

Rearrangement of pinacol dibromide by silver oxide in the presence of water.- This reaction was investigated for comparison with the one above, done in anhydrous conditions, to see if the presence of water furthered the extent of the rearrangement. For this work it was desired to have a solvent for pinacol dibromide that was also miscible with water and one that would still allow the use of Nessler's reagent for determining the pinacolone. A solvent which would conform to all of the above restrictions could not be found. It is interesting to note some of the solvents that were tried and the reasons for their rejection. Alcohol not only is oxidized by the alkaline Nessler's reagent precipitating mercury, but it also dissolves any pinacolone precipitate which may be present. Acetone was rejected because it reacts with Nessler's solution. Dioxan (diethylene oxide) enters into no reaction with Nessler's solution but will dissolve any pinacolone precipitate. Carbitol (monoethyl ether of diethylene glycol) has a free hydroxyl group in its molecule and is attacked by Nessler's solution, and is therefore useless. Ether is the only solvent we found which

would do; so in these determinations we used ether saturated with water.¹ If ordinary ether is used in this work it must be shaken with Nessler's reagent so that any impurity which may react will be removed. Pure ether does not react with Nessler's reagent. Because of the change in conditions a new calibration curve had to be made. This is necessary for every change in procedure because of the highly empirical relation which exists between the weight of Nessler's precipitate and the concentration of the solution from which it is obtained. Ether saturated with water was used in the determination. With wet ether the precipitation of the pinacolone derivative is much more rapid and a larger amount of the precipitate is formed. This was observed when the precipitates for the calibration curve were obtained.

In the rearrangement of pinacol dibromide the action of the silver oxide was impaired because it was wet and packed into large concretions which reduced its reacting surface. Even with this reduced surface it was found that in some of the attempts rearrangement had proceeded as far in twenty-four hours as it had in fifty-four hours in the case of rearrangement in anhydrous conditions. The data which illustrate this point are given in the experimental part which follows.

¹At 22°, 100 cc. of ether dissolves 2.93 cc. of water. A. Seidell, "Solubilities of Inorganic and Organic Compounds," p. 297, 2nd ed. (1919).

IV. EXPERIMENTAL PART

Preparation of anhydrous pinacol, $(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{OH})\text{C}(\text{CH}_3)_2$.

Pinacol hydrate was prepared from acetone by reduction with magnesium and mercuric chloride.¹ It contains six molecules of water and was dehydrated according to the method developed by K. H. Adams.² The hydrate (500 grams) was placed in a two liter round bottom flask connected in the ordinary manner to a condenser and a receiving flask for distilling in vacuum. The hydrate was then heated to about 80° and submitted to intermittent application of reduced pressures. A filter pump was used for this purpose and the vacuum broken by means of a stopcock in the line. This process removes heat from the pinacol by evaporation of the water faster than it can be supplied by the 80° bath, and the loss due to sublimation is cut down. After most of the water had been removed by this method the residue was transferred to another distilling flask and distilled under atmospheric pressure. The fraction boiling from 172°-175° is pure enough for most purposes.

The preparation of pinacolone, $(\text{CH}_3)_3\text{C}-\text{CO}(\text{CH}_3)$.- Pinacol (150 grams or 250 grams of the hydrate) is distilled with 450 grams of 6 N sulfuric acid until the upper layer of the distillate does not increase in volume. The pinacolone (upper layer) is separated from the water layer and is dried over calcium chloride. It is then fractionally distilled and the portion which boils over

¹Roger Adams, "Organic Synthesis" (New York: John Wiley and Sons 1925), V, 87.

²K. H. Adams, loc. cit., p. 27.

the range of 103-107° is collected.¹ The pinacolone used in this work had a boiling point range of 105.5-106.5°,²

The preparation of tetramethyl ethylene dibromide,
(CH₃)₂CBBrCBr(CH₃)₂.- Pinacol dibromide has been described and prepared by a number of investigators. Pawlow³ made it by the addition of bromine to tetramethyl ethylene.

(CH₃)₂C C(CH₃)₂ Br₂ (CH₃)₂CBBrCBr(CH₃)₂
He reported that the product melted above 140° at which temperature decomposition began. Couturier⁴ made the dibromide by treating anhydrous pinacol with phosphorus tribromide. Two methods were used to prepare this compound for the present work. The first one which is described by Ayers,⁵ consists in the passage of hydrogen bromide through 100 grams of molten anhydrous pinacol. The reaction mixture is kept cold by an ice bath. The colorless liquid becomes viscous and then turns to a greenish yellow color. After some time a white precipitate appears which becomes more granular as hydrogen bromide is absorbed. The gas is passed in for about three hours or until the mixture showed no tendency to become warm due to a continued reaction. At this point the liquid is decanted and the crystals are kneaded with ice water until the water is no longer colored. The mass of crystals is then poured on a Buchner funnel and sucked dry. The amount of dibromide obtained was 106 grams. This is 51 per cent of the theoretical yield. This preparation works very well, but it is slow and it

¹Roger Adams, op. cit., 5, 91.

²The boiling point is 106.2 according to the "International Critical Tables" (New York: McGraw Hill Book Co., 1926), 1, 202.

³Pawlow, Ann., 196, 124 (1879).

⁴Couturier, Ann. Chim. Phys., (6), 26, 444 (1892).

⁵Ayers, loc. cit.

is surpassed by the following modification of Thiele's¹ method in which molten anhydrous pinacol is treated with a concentrated aqueous solution of hydrogen bromide. This method is much easier to carry out than Ayers' and it gives a greater yield, but it is necessary to adhere closely to the following specifications. An aqueous solution of hydrogen bromide approximately 65 per cent in strength (65 grams of hydrogen bromide in 100 grams of solution) or of 1.78-1.79 specific gravity is added slowly to molten pinacol. This reaction mixture is maintained at a temperature below 40°. Precipitation of the dibromide takes place almost immediately but if the mixture is allowed to stand over night we found the yield was greater. When the precipitation is completed the liquid is decanted from the waxy mass of dibromide and this residue is washed well with ice water, then sucked dry on a Buchner funnel. This crude mass when recrystallized fractionally from anhydrous ether gives long transparent needles melting sharply at 172°. All the samples of dibromide used in this work melted from 171.7-172°. Wheeler lists the work of many observers on this compound and gives melting points that range from 140-190°.² Couturier³ gives the melting point as 173°. We found that if the needle-like crystals mentioned above are sublimed, the melting point of the crystalline sublimate is still 172°.

Ordinary 'concentrated' hydrogen bromide (40%) will not give the dibromide. For 30 grams of pinacol, 38.8 c.c. of the 65 per cent solution of hydrogen bromide are needed theoretically but a large excess of the hydrogen bromide is necessary for the reaction. It was found that 100 c.c. of the 65 per cent solution

¹ Thiele, Ber., 27, 455 (1894).

² Wheeler, Am. Chem. J., 20, 150 (1898).

³ Couturier, Ann. Chim. Phys., (6), 26, 445 (1892).

were sufficient to react with 30 grams of pinacol to give 42 grams of the dibromide or a 67 per cent yield. Thiele states that the hydrate of pinacol may also be used. We found that the yields were extremely poor in this case and therefore recommend only the use of anhydrous pinacol.

Because of the large amounts of hydrogen bromide used in this preparation it was made catalytically from hydrogen and bromine by a method that is being developed by Professor W. C. Johnson and Mr. A. E. Sidwell in this laboratory: Hydrogen, from a storage tank, is passed through bromine in the dark at about 40° and the resultant mixture is passed over platinized silica gel maintained at 350-400°. The hydrogen bromide thus formed is passed through a column of red phosphorus on glass beads to remove any unchanged bromine. The gas is then led through gas wash bottles filled with water and kept cold by salt-ice baths. One pound of bromine may be converted into hydrogen bromide very efficiently in 20-25 minutes. Unused hydrogen escapes from the train at the rate of about 1500 c.c. a minute.

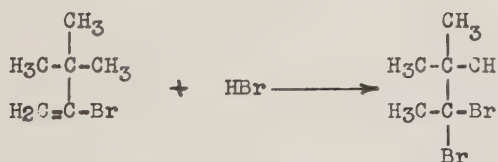
Preparation of pinacolone dibromide, $(\text{CH}_3)_3\text{C}-\text{CBr}_2(\text{CH}_3)$.- Pinacolone dibromide has been described in the literature by two writers. Couturier¹ prepared it from phosphorus pentabromide and pinacolone. It is difficult to prepare and the yields are extremely poor; so most of Couturier's work was done with an analogous compound made from phosphorus pentachloride and pinacolone which can be obtained in larger amounts and is more stable. Faworsky² modified Couturier's method and made the following statements about the preparation of pinacolone dibromide. The reaction of phosphorus pentachloride and pinacolone consists exclusively in the

¹Couturier, Ann. Chim. Phys., (6), 26, 450 (1892).

²Faworsky, J. prakt. Chem., 88, 669 (1913).

replacement of the carbonyl oxygen by chlorine to obtain the crystalline dichloride. When phosphorus pentabromide reacts with pinacolone the reaction goes in two ways. The first reaction is similar to phosphorus pentachloride and a replacement of the carbonyl oxygen by two bromine atoms takes place to give a crystalline dibromide. The second reaction is a substitution of bromine atoms for hydrogen to give mono and dibromo derivatives, with the evolution of hydrogen bromide. Faworsky's modification employs a steam distillation for the isolation and purification of the pinacolone dibromide. This is an improvement over Couturier's method but still the yields are low.

Because large quantities of hydrogen bromide are evolved in the reaction it was suggested that the reaction be run in a bomb tube to aid in driving the following equilibrium toward the formation of the dibromide.



In the case of the preparation of the corresponding dichloro compound from phosphorus pentachloride and pinacolone, Delacre reports that when the reaction takes place in the cold a liquid chloride of the formula $(\text{CH}_3)_3\text{C}-\text{CClCH}_2$ forms 30-40 per cent of the reaction mixture.

The reaction in the sealed tube was to be run at a low temperature and, all the hydrogen bromide being present, there would be a greater chance for saturation of the double bond indicated in the above equation. This method combined with the steam distillation suggested by Faworsky gave better yields than were

ever obtained by the older methods. Phosphorus pentabromide (22 grams) was placed on the bottom of a heavy walled pyrex tube and then a tube containing 5 grams of pinacolone was slid down the wall of the tube so that there was no contact between the two substances. The tube is then sealed off and after being thoroughly chilled it is tipped so that the two compounds will react. The bomb is kept in a salt-ice bath for two hours or until all of the phosphorus pentabromide has disappeared. It is slowly brought to room temperature and allowed to stand over night. Before the tube is opened, its contents are frozen by means of solid carbon dioxide in an acetone bath. The reaction mixture is poured immediately into ice water to decompose the phosphorus compounds. A heavy brown oil-like substance separates from the water. When the entire mixture of oil and water is steam distilled, the dibromide solidifies on the walls of the condenser. The crystals are transferred to a Buchner funnel and sucked dry. If further purification is desired the product may be recrystallized from ether. A sample purified in this manner melted in a closed tube at 191° . The yield is 2 grams or 16 per cent. Pinacolone dibromide is a very volatile solid and a powerful lachrymator. It is difficultly soluble in water and in aqueous alkali even at 100° .

The corresponding pinacolone dichloride, $(\text{CH}_3)_3\text{C}-\text{Cl}_2\text{CH}_3$, can be made by the dropwise addition of pinacolone to phosphorus pentachloride. The reaction mixture is kept in an ice bath during the addition of the pinacolone. The phosphorus compounds are decomposed by water and the entire mixture is then steam distilled to isolate the dichloride. This compound is more stable than the dibromide and may be obtained in 40 per cent yields.

Preparation of isobutyl acetylene from bomb contents,
 $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{CH}$. Benzene solutions of pinacol dibromide (1-2 grams)

were heated in sealed pyrex tubes for 6 hours at temperatures which varied for different attempts from 150°-250°. After this heat treatment the contents of the bomb were frozen, the tubes then opened and alcoholic potassium hydroxide (excess over the calculated amount for 2 mols of hydrogen bromide) was added with sufficient alcohol to make a homogeneous mixture. The tubes are resealed and heated at 160° for 15 hours. If any pinacolone dibromide is present in the bomb due to a rearrangement of the symmetrical dibromo compound it will be changed to isobutyl acetylene. This reaction was demonstrated by the use of pinacolone dibromide or a mixture of one fourth pinacolone dibromide and three fourths pinacol dibromide in benzene and treatment of this mixture with alcoholic potassium hydroxide at 150° for 15 hours. The acetylene could be isolated from this mixture by means of its silver salt. The copper salt of the acetylene, made from cuprous ammonium chloride, is too soluble in benzene to be isolated. The silver salt, however, may be made in benzene solution by addition of silver ammonium nitrate and then addition of alcohol until the benzene and water layers are homogeneous. It is a white crystalline solid that is easily handled. The acetylides may be heated in a melting point tube to 230 with no evidence of change. No acetylene was ever isolated from a heated benzene solution of pinacol dibromide which was treated with alcoholic potassium hydroxide.

Rearrangement of pinacol dibromide by silver oxide.-

Samples of the dibromide in an ether solution were shaken at room temperature with an equivalent amount of silver oxide to react with the two atoms of bromine. The reaction mixture was shaken in an electric shaking machine and samples for analysis were taken at various times as the reaction progressed. It was found most convenient to shake the reaction mixture in a brown glass bottle

stoppered with a tightly fitting cork covered with tin foil and sealed with De Kohtinsky cement. Samples of 25 c.c. were taken by means of a pipette whose tip was covered with a fine filter to keep out silver oxide and silver bromide. This sample was then run into a glass stoppered Erlenmeyer flask containing 75 C.C. of Nessler's solution. This mixture was shaken intermittently for 2 hours to precipitate the ketone and then heated on a steam bath to drive off the ether and unchanged dibromide, also to coagulate the precipitate. The precipitate was collected on a porous bottom Gooch crucible and brought to constant weight by drying over phosphorus pentoxide in a vacuum desiccator.

The Nessler reagent used in the analysis was prepared from 84 grams of potassium iodid and 3.4 grams of mercuric chloride dissolved in 800 c.c. of distilled water. A saturated solution of mercuric chloride is then added to this solution until a permanent red precipitate formed. To this mixture is added a solution of 385 grams of fused potassium hydroxide in one liter of water. Water is then added until a volume of 2400 c.c. is reached and finally more saturated mercuric chloride solution until a permanent red-yellow precipitate formed.

The following tables of data show the progressive change of pinacol dibromide into pinacolone by means of silver oxide. The heading of each table gives the amounts of pinacol dibromide and of silver oxide that were shaken in the indicated volume of ether. Column I (Time in Hours) shows the time from the beginning of the shaking until the sample of 25 c.c. was taken, or the time of contact between the silver oxide and the ether solution of the dibromide before analysis. Column II (Wt. of Nessler's Precipitate) shows the weight of the precipitate obtained from the 25 c.c. sample taken at the indicated time. Column III

(Wt. Per cent of Pinacolone) shows the amount of pinacolone in the solution (strength of solution) at the time indicated in Column I. This value is read from the calibration curve when the weight of precipitate from the solution in question is known.

An appendix to the first table shows the strength of the pinacolone solution, in mols, that would result if all of the dibromide had been converted into pinacolone. This value is also expressed as weight per cent solution for comparison with the values given in Column III of the table. The weight of the Nessler precipitate, which would result if the total theoretical amount of pinacolone had been precipitated, is also given. This value may be read from the calibration curve since the strength of the theoretical solution is known. This weight may be compared with the weights given in Column II for the extent of rearrangement of pinacol dibromide into pinacolone. The values given in the appendix, i.e. the theoretical amount of pinacolone and the corresponding weight of precipitate, apply to all of the following tables; the ratio between the dibromide, silver oxide and volume of ether used being maintained throughout.

TABLE I*

1.255 GRAMS OF DIBROMIDE IN 150 C.C. ETHER
1.255 GRAMS OF SILVER OXIDE

Time in Hours	Wt. of Nessler's Precipitate	Wt. Per cent of Pinacolone
2	0.0111	
3	0.0366	0.04
6	0.0594	0.056
28	0.0763	0.068

*Theoretically possible..... 0.034 M solution
0.48 per cent solution
0.572 grams of precipitate

TABLE II

1.883 GRAMS OF PINACOL DIBROMIDE 225 C.C. ETHER
1.883 GRAMS OF SILVER OXIDE

Time in Hours	Wt. of Nessler's Precipitate	Wt. Per cent of Pinacolone
2	0.0640	0.060
3.5	0.0631	0.060
4.75	0.0715	0.066
7.5	0.0911	0.080
9	0.1056	0.090
30	0.2238	0.176

TABLE III

1.869 GRAMS OF PINACOL DIBROMIDE IN 225 C.C. ETHER
1.869 GRAMS OF SILVER OXIDE

Time in Hours	Wt. of Nessler's Precipitate	Wt. Per cent of Pinacolone
2.5	0.0520	0.052
4.75	0.0745	0.068
6	0.0829	0.074
7	0.0877	0.078
30	0.1555	0.126
54	0.2569	0.200

TABLE IV

1.869 GRAMS OF PINACOL DIBROMIDE IN 225 C.C. ETHER
1.869 GRAMS OF SILVER OXIDE

Time in Hours	Wt. of Nessler's Precipitate	Wt. Per cent of Pinacolone
2.5	0.0405	0.044
4.75	0.0502	0.050
6	0.0710	0.066
8	0.0846	0.076
30	0.1147	0.096
54	0.1692	0.136

TABLE V

1.869 GRAMS OF PINACOL DIBROMIDE IN 225 C.C. ETHER
1.869 GRAMS OF SILVER OXIDE

Time in Hours	Wt. of Nessler's Precipitate	Wt. per cent of Pinacolone
2.5	0.0325	
4.75	0.0517	0.520
6	0.0630	0.060
7	0.0646	0.060

The following tables are analogous to the preceding ones. These, however, show the progressive change of pinacol dibromide into pinacolone in the presence of water, i.e. in a solvent of ether saturated with water. The columns here have the same significance as the preceding ones. Each table has an appendix which shows the amount of silver bromide recovered when the reaction is stopped. This is an indication of the amount of pinacol dibromide that remains unchanged, since silver bromide may be formed from pinacol dibromide as it is changed into tetramethyl ethylene oxide, $(\text{CH}_3)_2\text{C} \begin{array}{c} \diagup \diagdown \\ \text{O} \end{array} \text{C}(\text{CH}_3)_2$, or as it is changed into pinacolone.

The silver bromide was recovered by evaporation of the ether and heating the residue until the volatile pinacol dibromide had been driven off. The silver oxide and silver bromide mixture which remained was treated with nitric acid and heated to coagulate the silver bromide. The precipitate was transferred to a porous bottom Gooch crucible, washed well and dried until its weight was constant.

In each of the following runs 1.869 grams of pinacol dibromide was dissolved in 225 c.c. of wet ether and shaken at room temperature with 1.869 grams of silver oxide.

TABLE VI*

Time in Hours	Wt. of Nessler's Precipitate	Wt. Per cent of Pinacolone
1	0.0136	less than 0.01
2	0.0170	" " 0.01
4.75	0.0520	" " 0.01
24	0.1421	0.033

*0.7421 grams of AgBr recovered
2.877 grams is the theoretical amount of AgBr obtainable from 1.869 grams of pinacol dibromide.

TABLE VII*

Time in Hours	Wt. of Nessler's Precipitate	Wt. Per cent of Pinacolone
1	0.0187	less than 0.01
2	0.0271	less than 0.01
4.75	0.0565	less than 0.01
7.25	0.0828	less than 0.01
24	0.2450	0.112

*0.7856 grams of AgBr recovered.

TABLE VIII*

Time in hours	Wt. of Nessler's Precipitate	Wt. Per cent of Pinacolone
1	0.0173	less than 0.01
2	0.0212	" " 0.01
3.5	0.0274	" " 0.01
4.75	0.0539	" " 0.01
6.25	0.0706	" " 0.01
24	0.3606	0.200

*1.021 grams of AgBr recovered.

Calibration curves used in the analyses.- The amount of Nessler's precipitate obtained from pinacolone in a solution is not directly proportional to the amount of pinacolone in the solution. However, a calibration curve can be made which will show the deviation from the straight line function.. The following method was used to obtain this curve: A definite amount of pinacolone weighed in a sealed ampoule was placed in a weighed glass stoppered Erlenmeyer flask together with a calculated amount of ether to make a solution of given molality. The flask, tightly stoppered, was then weighed to obtain the weight of the ether. Knowing the weight of the pinacolone and the weight of the ether,

the weight per cent of the solution could be calculated, i.e., the grams of pinacolone divided by the total weight of the solution multiplied by one hundred. Sufficient solution was made in each case to have two 25 c.c. samples of the same composition for check determinations. Each of the 25 c.c. samples was added to 75 c.c. of Nessler's reagent contained in glass stoppered Erlenmeyer flasks. This mixture was shaken periodically for two hours and then heated on a steam bath to drive off the ether and coagulate the Nessler precipitate. After cooling, the precipitate was transferred to a porous bottom Gooch crucible and dried to constant weight over phosphorous pentoxide in a vacuum desiccator. The weights of the Nessler precipitate are then plotted as ordinates against the weight per cent composition of the various solutions. The following table gives the data obtained from 25 c.c. portions of the various ether solutions with 75 c.c. of Nessler's reagent. Curve number 1 is plotted from these values.

TABLE IX

Approx. Molality of Pinacolone	Weight Per Cent of Pinacolone	Weight of Nessler's Precipitate	Average Weight of Precipitate
0.002	0.033	0.0300 0.0318	0.0309
0.005	0.070	0.0831 0.0827	0.0829
0.01	0.148	0.1600 0.1840	0.1720
0.02	0.279	0.3646 0.3701	0.3674
0.03	0.418	0.5088 0.5286	0.5187
0.05	0.701	0.7323 0.7414	0.7368
0.055	0.774	0.7806 0.7636	0.7721
0.065	0.907	0.7927 0.8290	0.8108
0.090	1.23	0.8488 0.8646	0.8567

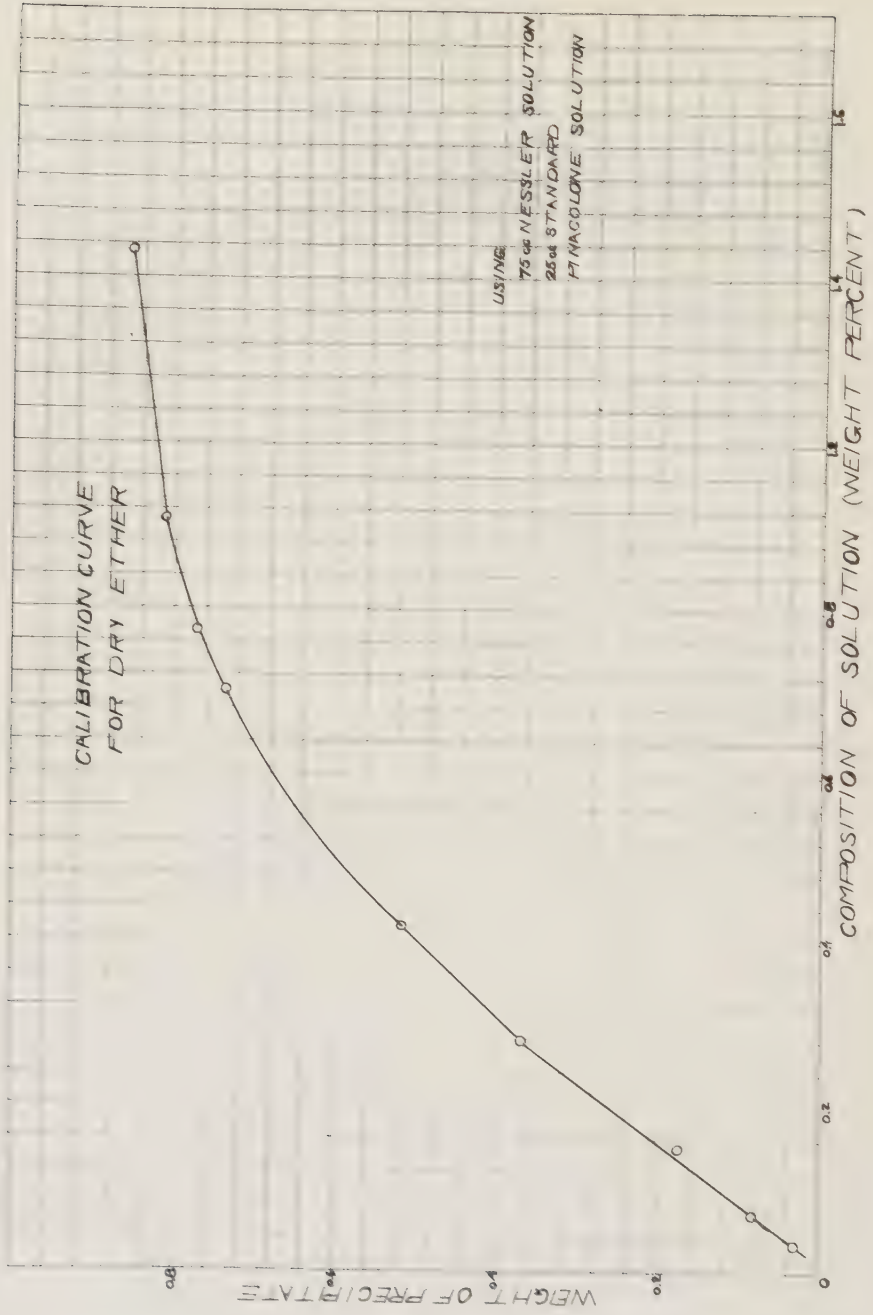


Figure 1

Because of the highly empirical nature of the estimation of pinacolone by Nessler's reagent any change in the method of analysis or in the materials used demands a new calibration curve. The data for the calibration curve must be obtained from the same stock of Nessler's solution that is to be used in the analysis and the work must be carried out under the same conditions. The following data was obtained for the calibration curve using wet ether and 25 c.c. samples of the pinacolone solution with 75 c.c. of Nessler's reagent.

TABLE X

Approx. Molality	Average Weight of Precipitate	Weight Per cent of the Solution
0.001	0.0853	0.014
0.001	0.0875	0.014
0.0015	0.1101	0.0206
0.002	0.1367	0.029
0.0035	0.1608	0.048
0.005	0.1894	0.070
0.0065	0.2135	0.088
0.008	0.2416	0.109
0.0095	0.2725	0.130
0.015	0.3634	0.207
0.017	0.4077	0.235
0.019	0.4453	0.260

CALIBRATION CURVE
FOR WET ETHER

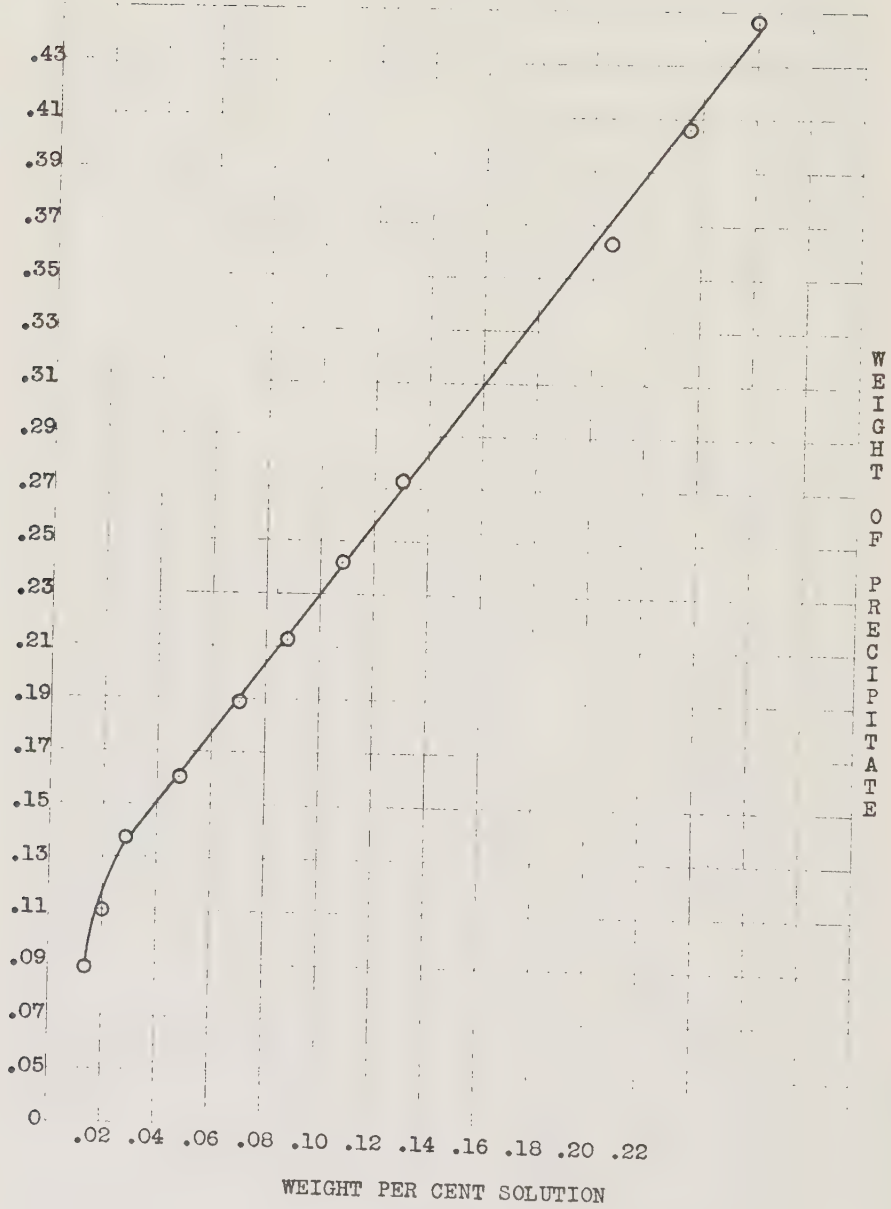


Figure 2

SUMMARY

1. The Stieglitz theory of the pinacol-pinacolone molecular rearrangement has been presented and applied to interpret the rearrangement of pinacol dibromide.

2. An attempt was made to rearrange pinacol dibromide into pinacolone dibromide by pyrolysis. The molecule was disrupted in the reaction and therefore no rearrangement could be detected.

3. An explanation is offered for the difference in the ease of rearrangement of the bromohydrine, $(\text{CH}_3)_2\text{C}(\text{OH})\text{CBr}(\text{CH}_3)_2$, and the dibromide, $(\text{CH}_3)_2\text{CBrCBr}(\text{CH}_3)_2$, in which each molecule loses bromine as bromide ion thus forming the rearranging entity.

4. Pinacol dibromide was rearranged in anhydrous ether by means of silver oxide.

5. Quantitative determinations were made on the progress of the rearrangement reaction.

6. The rearrangement of pinacol dibromide by silver oxide in water saturated ether was compared to the above reaction.

7. An improved preparation of pinacolone dibromide is described.

